

# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### Improved Dewaxing and Dehazing Process

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the dewaxing of middle distillates and petroleum hydrocarbon oils to prepare premium fuel, heating, lubricating and diesel oils. More particularly, the present invention relates to improving the cloud, pour and haze properties of petroleum hydrocarbon oils, such as lubricating oils, diesel oils, transformer oils, oils boiling in the kerosene range and adapted for use as jet fuels, and other oils that are subject to low temperatures. Generally, the present invention relates to a novel process for obtaining high degree of wax removal from these compositions by means of solid adsorbents.

The unsatisfactory performance of lubricating oils and diesel fuels at cold temperatures and in cold climates has been a problem that has been with the petroleum industry a long time. The problem has been traced to small amounts of wax in the oils. Below a critical temperature, the cloud point of the fuel, filter blockage occurs, with resultant fuel starvation of the engine in the case of diesel fuels. In the case of lubricating oils, the precipitated wax increases the viscosity of the oil and makes proper lubrication difficult.

In the refining of petroleum hydrocarbon oils, it is known to segregate paraffin waxes from so-called paraffin distillates, waxy lubes and the like. The segregation of these waxes is secured by a number of processes, such as by chilling to effect crystallization, chilling in the presence of a solvent such as a liquefied normally gaseous hydrocarbon for example, propane, or solvent extraction, for example, with a ketone. These conventional dewaxing operations are not always feasible nor satis-

[Price 3s. 6d.]

factory. These are expensive processing steps and the costs are not always justified. Many refineries produce lubricating oils from crudes having a low wax content, such as naphthenic crudes. The amount of wax present of the order of 0.1—4% by weight, is not enough to warrant a conventional dewaxing treatment, which includes the use of expensive solvents, compressors, refrigerants and filtration equipment.

Other processing steps, such as clay treating, acid treating, and phenol extraction do not have a significant effect on the haze point which is defined as the lowest temperature at which a lube oil will remain clear for an indefinite period.

The cloud point is the temperature at which paraffin wax or other solid substances begin to crystallize out or separate from solution when the oil is chilled under definite prescribed conditions.

As little as 0.1 to 0.5% by weight of suspended wax crystals in lubricating oils causes haze, at low temperatures, and only 0.15% by weight of wax will raise the haze point 30° F.

It is therefore the principal purpose of the present invention to set forth a novel method of removing wax particles from petroleum hydrocarbon oils particularly middle distillates lubricating oils, diesel oils and jet fuels.

It is a still further object of the present invention to set forth a method of removing small amounts of finely divided wax crystals from oils initially containing only small amounts of wax.

It has now been found that petroleum hydrocarbon oils having excellent haze, cloud and pour points may be produced by contacting the said oil containing waxy and/or forming constituents at elevated temperatures with certain naturally occurring or synthetic crystalline zeolites known as molecular sieves. These zeolites have innumerable pores of uniform size, which may vary in diameter from 4 Angstrom units to 13 or more, but it is a property of these zeolites that any particular sieve has pores of a completely uniform size.

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For the present invention, pore openings of from 4.5 to 5.5 Angstrom units are used for removing wax from the petroleum hydrocarbon oils. These pore openings are large enough to admit freely the predominantly straight chain wax molecules, but will not admit the isomeric paraffins constituting the bulk of the oil being dewaxed.

- Smaller openings exclude most normal hydrocarbons while larger openings would not exclude the isoparaffins, thus adversely affecting the selectivity of the crystalline zeolite composition.

- The present invention consists of a process for removal of waxy and/or haze forming constituents from petroleum hydrocarbon oils characterized by passing a stream of said oil to an adsorption zone, contacting said stream in said zone at a temperature greater than 300° F. with an adsorbent having uniform pore openings of from 4.5—5.5 Angstroms and withdrawing a purified oil from said zone.

- The reaction is preferably carried out at temperatures within the range of from 400° to 800° F. At temperatures of less than 300° F. little wax removal is realized whilst at temperatures above 800° F. secondary reactions such as cracking occur.

- Among the natural zeolites having this sieve property may be mentioned chabasites and analcite. Synthetic zeolites with molecular sieve properties are also well known. Zeolites vary somewhat in composition, but generally contain the elements of silicon, aluminium and oxygen as well as an alkali and/or an alkaline earth element, e.g. sodium and/or calcium. The naturally occurring zeolite, analcite, for instance, has the empirical formula



- It is known that the sodium is replaceable by calcium to yield, on dehydration, a molecular sieve having the formula



- Similarly, a synthetic molecular sieve zeolite having the formula  $4 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4 \text{SiO}_2$  is also known.

- The sieves may be regenerated by such means as steam desorption at elevated temperatures up to 1000° F., at reduced pressures, if desired, or by treatment with a fluid more polar than the adsorbed material, or by passage through the sieve bed of an inert gas such as nitrogen, methane,  $\text{CO}_2$  or  $\text{NH}_3$ , or by stripping with refinery gas streams preferably containing olefinic constituents such as ethylene propylene or butylenes. If desired, the sieve may be regenerated completely by heating to a temperature not above 1000° F. in the presence of air or steam.

- Aluminosilicates of high dewaxing activity may be prepared by the controlled mixing

under carefully controlled conditions, of a sodium silicate, and preferably sodium metasilicate, with sodium aluminate to form a crystalline product which is subsequently base exchanged with a metallic ion such as calcium. The sodium silicate must have a ratio of soda to silica of at least 0.8/1. Water glass or sodium silicates having a lower  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio do not form the selective adsorbent crystals unless subjected to extended heat soaking or crystallization periods.

Sodium aluminates having any ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  in the range of 0.8/1 to 3/1 preferably 1/1 to 2/1 may be employed; a sodium aluminate having a ratio of soda to alumina of 1.5/1 being particularly preferred.

The mixing of the sodium metasilicate and aluminate must be carried out in a manner allowing formation of a precipitate having a uniform composition. A preferred method is to add the aluminate to the metasilicate at ambient temperatures using rapid and efficient agitation to make a homogeneous paste. Thereafter the mixture is heated to about 180° to 215° F. for a period of about 0.5 to 3 hours or more. The crystals are also formed at lower temperatures, but a greater length of time is needed. However, above about 250° F., the crystalline composition having the desired uniform size pore openings are not obtained.

An important step in the preparation is to have the crystallization take place in an alkaline medium, at a pH greater than about 12. At lower pH levels, crystals with the desired properties are not as readily formed.

After the crystallization step, the crystals are washed and added directly to a solution of a calcium salt, such as an aqueous calcium chloride solution. After a contact time of 5 minutes to an hour, the final product, now having a uniform pore opening of about 5 Angstroms, is filtered, washed, and activated by calcination at about 700° to 900° F.

In accordance with one mode of the present invention, this crystalline composition in which about 65% or more of the sodium has been exchanged for calcium, is employed in dewaxing middle distillates and lube stocks.

The dewaxing may be carried out (1) in the vapor phase at reduced pressure or with a non-adsorbable carrier oil, or (2) in liquid phase at elevated temperature or with the heavy oil diluted with a non-adsorbable oil, i.e., an oil whose molecules have diameters greater than 5 Angstrom units. A fixed bed or slurry operation may also be employed.

The process of the present invention may be more readily understood by reference to the accompanying drawings illustrating an embodiment of the same.

Referring specifically to Figure 1, a waxy distillate boiling in the gas oil range or above is passed via line 2 to contacting zone 4. Finely divided calcium sodium aluminosilicate having a uniform pore diameter of about 5 Angstroms

is passed into vessel 4 via line 6. Vessel 4 is provided with efficient agitation and maintained at a temperature of about 300° to 700° F., preferably 400° to 650° F., and oil-crystal contacting is maintained for a period sufficient to adsorb the wax and/or haze forming constituents; the residence period varies with the per cent. wax content, and may be from 5 to 60 minutes. If desired, a non-adsorbable hydrocarbon fraction such as an iso- or a cycloparaffin or aromatic may be admitted through line 8 to act as oil diluent and contact promoter, particularly where the oil has a high viscosity.

The slurry of oil and adsorbent, with or without added diluent, is then passed to filtration zone 12, where the adsorbent is removed from the liquid in a conventional manner. Additional non-adsorbable hydrocarbon may be employed as a wash liquid, being introduced via line 14. The filtrate, consisting of dewaxed oil and diluent, is withdrawn through line 16, separated by a simple distillation into a diluent and a diluent-free heavy fraction, and the diluent is recycled via line 22, while the dewaxed oil is recovered through line 20.

The wax-containing adsorbent is now transferred to a regeneration zone. In the embodiment shown in Figure 1, the adsorbent is passed to hot water treating zone 26 where, at a temperature of from 150° to 300° F., and pressures, sufficient to maintain the water in the liquid phase the sieve is regenerated, the more polar water molecules replacing the adsorbed hydrocarbon molecules in the adsorbent interstices. The molten wax forms an upper layer and is withdrawn through line 28 for recovery and purification in a manner known per se. The aqueous slurry of wax-free adsorbent is passed to filtration zone 32. The adsorbent is passed to calcination zone 38 where, at a temperature of from about 500° to 900° F., the water molecules are expelled from the interstices and pores, and the product is ready for further dewaxing, and so is recycled via line 40 to contacting zone 4.

Instead of water, however, the wax may be removed in zone 26 by other compounds for which the adsorbent has a greater affinity than it has for wax molecules, for example, olefins such as propylene or butylenes, or lower boiling normal paraffins may be employed. Similarly, normal primary alcohols such as methanol, ethanol and butanol, may be employed.

#### EXAMPLE 1.

A crystalline aluminosilicate adsorbent

having 5 Angstrom pore openings was synthesized as follows:

1. Reagents: Dissolve sufficient metso- granular sodium meta-silicate (available from the Philadelphia Quartz Company) in distilled water to give a 19.1% by weight concentration of  $\text{Na}_2\text{SiO}_3$ . Place 250 grams of this material in the reaction beaker. In another beaker, weigh out 100 grams of a commercially available sodium aluminate solution containing 42% sodium aluminate.
2. Mix the two solutions at room temperature by pouring the aluminate into the silicate while stirring vigorously.
3. Quickly raise the temperature of the above mixture to 200° F. by placing the beaker in a constant temperature bath and stirring rapidly. Maintain this slurry at this temperature for three hours.
4. Pour the product on to cracked ice to stop reaction.
5. Filter with suction and wash the filter cake with one liter of distilled water.
6. Dry the product overnight at 200° F. Analysis of this material showed the composition to be  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ .
7. Convert the above sieve product (4 Angstrom Type) to the calcium form (5 Angstrom) with an excess of calcium chloride solution. This exchange is carried out by soaking 1 part (by weight) of the 4 Angstrom powder in 10 parts of 20% by weight calcium chloride solution. After soaking for approximately one hour, the adsorbent powder is filtered, washed by reslurrying several times in water, filtered, dried overnight in an oven at 225° F., and then calcined for two hours at 850° F. Chemical analysis showed that 70% of the sodium had been replaced by calcium.

#### EXAMPLE 2.

A gas oil having a boiling range of 354° to 700° F. (ASTM Distillation), an API gravity of 31.8 and a pour point of 38 was slurried with the powdered material prepared according to Example 1 in the proportions of 7.3 and 14.6 pounds powder per gallon of oil, and heated to 575° F. The slurry was then cooled to 180° F. and filtered, the filter cake washed with benzene, and the benzene removed from the dewaxed oil by distillation. The dewaxed oil was recovered with a volumetric yield of 85.9% and had an API gravity of 29.5.

TABLE I  
Adsorbent Treating of Heavy Gas Oil For Wax Removal

Test No.	Adsorbent Treat		Wax Removed, wt. %	Pour Point of Treat Oil
	Lb. Sieve/Gal. Oil	Temp. °F.		
Feed	0	—	0	38
Slurry Treats				
384	7.3	200	1	—
383A	7.3	315	1.2	—
378A	7.3	400	11.2	—
385A	7.3	500	14.1	—
386	7.3	575	14.5	—
383B	14.6	315	1.2	—
378B	14.6	400	13.7	—
385B	14.6	500	14.1	—
Fixed-Bed Partial Vapor Phase Treat				
372	11.5	400	14.0	—30

It will be noted that at 315° F. and below, only about 1 wt. % of wax, based on total oil, was removed, while at 400° F., 11.2 to 13.7 wt. % is readily adsorbed by the selective adsorbent. These data show a very sharp and critical division of less than 85° F. between operable adsorption temperatures and unsatisfactory contacting conditions. The same temperature effect was obtained at both the 7.3 and the 14.6 pounds per gallon treating level. A fixed bed treat made in partial vapor phase at 400° F. (Test 372) using benzene as a non-adsorbable carrier oil gave results quite similar to the slurry treats at the same temperature and comparable adsorbent/oil ratios. The pour point of this oil was reduced from +38 to -30.

#### EXAMPLE 3.

Table II below shows the improvement in pour point obtained when waxes are removed

from middle distillates at low pressures. To take advantage of the high selectivity at low pressures, it is desirable to employ a reduced pressure operation. Particularly desirable are pressures below about 50 mm. Hg. These pressures are readily obtained by condensation of the middle distillate product where no gas formation occurs. Since high temperature adsorption is accomplished by a certain amount of cracking and consequent gas formation, very low pressures are difficult to obtain. Thus, when temperatures above about 750° F. obtain in the adsorption zone, it is not desirable to employ pressures in the adsorption zone significantly below atmospheric. However, where lower adsorption temperatures are employed, pressures as low as 0.1 mm. mercury may be employed concomitantly as dictated by economic considerations.

TABLE II  
Sieving Middle Distillates  
Effect of Temperature

Pressure	Yield of dewaxed oil	Temp.	Pour Point Improvement
1 atm.	85.5%	800°F.	70°F.
1 atm.	85.5%	730°F.	30°F.
1 atm.	96%	800°F.	40°F.
1 atm.	96%	730°F.	10°F.

Effect of Pressure

Temp.	Pressure	Yield of dewaxed oil	Pour Point Improvement
730°F.	1 atm.	93%	15
730°F.	60 mm.	93%	15
730°F.	20 mm.	93%	20
550°F.	0.4 mm.	93%	30

Summarizing the relationship between vapor phase adsorption temperature and pressure, these are shown in Table III below:

TABLE III  
Adsorption Temperature, °F.\*      Approx. Adsorption Pressure, mm. Hg.

Case 1	730—850	760
Case 2	600—750	50
Case 3	500—600	1

\* Temperature limited by effect of cracking on product.

## EXAMPLE 4.

To illustrate another embodiment of the process, a naphthenic lubricating oil or diesel fuel is dewaxed in accordance with the present invention. For highest effectiveness of this embodiment of the process, the stock should have a wax content not greater than about 4% by weight, and preferably between 0.1 to 1.0% by weight.

With reference to the Figure 2, a liquid feed preheated to about 400° to 800° F. is admitted through line 101 to adsorption tower 108 which may be at a temperature of 400° to 800° F. Within the tower there is maintained a bed of molecular sieves of the type described in Example 1, which may be in a fixed bed or slurry form. The haze-conferring constituents are selectively adsorbed by the sieve and the effluent leaving by line 104 is substantially wax-free. The oil is passed into

the tower until wax appears in the effluent. This may be determined by haze or cloud formation tests. Then the desorbing gas or vapor is passed through line 105 into the column. The waxy constituents, fluid or vaporized, at the temperatures prevailing in tower 108, which, during the desorption step may be in the range of 400° to 1000° F., are desorbed almost completely, and are collected through product line 103. After desorption, the cycle is repeated and further wax-contaminated oil is passed through tower 108.

## EXAMPLE 5.

A sample of Tia Juana raffinate lube oil having a wax content of about .45% by weight was passed upwardly at a rate of 0.62 V/V/Hr. through a bed of molecular sieves of 5 Angstrom pore size. The improvement in the lube oil haze, cloud and pour point are readily apparent from the table below:

Treating Temp., °F.	Cloud Point, °F.	Haze Point, °F.	Pour Point, °F.
600	8	40	10
700	8	48	8
Feed	50	70	25

## EXAMPLE 6.

The cloud point and pour point of diesel fuel has been substantially reduced by treatment with a molecular sieve type adsorbent. For example, a sample of gas oil (500° to

750° F. boiling range) was treated with a molecular sieve of 5 Angstrom pore size at 800° F. and 0.3 V/V/Hr., with the following results:

	Yield	Cloud Point °F.	Pour Point °F.
Untreated	100	50	50
Treated	86	0	-25
	91	20	—

At the specification value of 20° F. cloud point, a yield of 91% was obtained.

## EXAMPLE 7.

A Tia Juana lube oil having a wax content of 0.32 wt. % was passed through the sieve at 0.5 w/w/hr. and at temperatures of 600°, 650°, and 700° F. A significant improvement in cloud point and haze point was obtained in each case as indicated in the table below.

About half of the wax was removed by the treatment. The remaining wax is probably predominately branched molecules. It can be

noted that the quality of the effluent remained good up to about 30 w/w. The amount adsorbed was found to be about 8 lbs. of wax per 100 lbs. of sieve.

Regeneration between cycles was carried out by burning with a refinery tail gas containing 2.5% by volume of oxygen and the temperature was maintained below 1000° F. during this operation. These regenerations were found to restore the adsorptive capacity without harming the sieve.

## STUDIES OF SIEVE DEHAZING OF EXTRACTED HEAVY TIA JUANA DISTILLATE

Run No.	1	2	3
Operation Conditions			
Temperature, °F.	650	700	600
W/W.Hr.	1/2	1/2	1/2
Total Hrs. on Absorption	53	82	93
Feed			
Inspections			
W/W	0-10 10-13 13-26 0-4 4-6 6-41 0-3 3-5 5-10 10-12 12-29 29-46		
Cloud, ASTM °F.	62 36-46 38-46 42-50 26 30 30-56 28 42 36 44 36-52 48-54		
Pour, ASTM °F.	+5 0 - +5 +5 +5 to +10 -10 -5 to -10 0 to -10 - - - - -		
Haze, °F.	<70 45 45 45 45 45 45 40 45 45 45 45-55 55-65		
Dewaxing @ 20°F.			
W/W	1 11 26 1 5 41		
Wax, Wt. %	0.32 0.16 0.13 0.20 0.16 0.18 0.18		
Sieve Regeneration by Burning			
Gas Rate, Cu. Ft./Min.	0.5	0.5	0.5
% Oxygen	1-2.5	1-20	1-20
Max. Temperature, °F.	760	1000	1000
Starting Temperature, °F.	700	825	825

It is further to be understood that instead of the natural or synthetic zeolites described as suitable for this purpose, other adsorbents having uniform pore openings of about 5  
5 Angstrom units may be employed. Thus, certain activated carbons have been found to have uniform pore openings of this size and may be used for this service.

The process of the present invention may  
10 be subject to many variations without departing from its scope. Thus, it may be desirable under certain circumstances to carry out both the adsorption and desorption in the vapor state. The sieves may be employed not only  
15 as a fixed bed or slurry but also in a fluidized solids type of operation. Also, since the solubility of wax in hydrocarbons decreases exponentially with the melting point of the wax, it may be desirable in some cases to re-  
20 move only the higher melting waxes from the diesel fuel or lube oil to lower the cloud and haze points. This may be done effectively by treating only the higher boiling fractions of the oil, i.e., those boiling in the range of 700°  
25 to 950° F. for lube oils, and 650° to 750° F. for diesel fuels, with a molecular sieve adsorbent. Normally, the cut point will be determined by the nature of the oil and the amount of improvement desired. Other modifications  
30 which can be employed include the introduction of the slurry of adsorbent into the trays of a fractionating tower wherein a lubricating oil fraction is being distilled. The settled wax-containing adsorbent may then be regenerated  
35 in the manner already described. Also, a lubricating oil may be simultaneously dewaxed and its viscosity index upgraded by employing, along with the selective adsorbent described, a second adsorbent having slightly larger pores,  
40 from 6 to 15, preferably 13 Angstroms, to remove aromatic impurities. The latter adsorbents are produced in a manner similar to the first named adsorbent except that the ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  in the reaction mixture is from  
45 3/1 to 10/1 and a somewhat longer heat soaking period is required.

#### WHAT WE CLAIM IS:—

1. A process for removal of waxy and/or  
50 haze forming constituents from petroleum hydrocarbon oils characterized by passing a stream of said oil to an adsorption zone, contacting said stream in said zone at a temperature greater than 300° F. with an adsor-

bent having uniform pore openings of from 4.5—5.5 Angstroms and withdrawing a purified oil from said zone. 55

2. A process according to claim 1 wherein the process is carried out at a temperature of from about 400 to 800° F.

3. A process according to claim 1 or claim 2 wherein said petroleum hydrocarbon oil contains from 0.1 to 4% by weight of wax. 60

4. A process as claimed in any one of claims 1 to 3 wherein said adsorbent is a crystalline metallic aluminosilicate. 65

5. A process according to claim 4 wherein said adsorbent is a crystalline sodium-calcium aluminosilicate.

6. A process according to claims 1 to 5 wherein a diluent hydrocarbon having molecules of a diameter greater than 5 Angstroms is passed into said contacting zone. 70

7. A process according to claims 1 to 6 wherein said adsorbent is regenerated after having been contacted with said hydrocarbon oil feed stream. 75

8. A process according to claim 7 wherein said adsorbent is regenerated by treatment with a fluid more polar than the adsorbed material. 80

9. A process according to claim 8 wherein said fluid is water and the regeneration temperature is within the range of from 150 to 300° F. and said adsorbent is thereafter calcined at a temperature of from 500° to 900° F. 85

10. A process according to claim 9 wherein said regenerated adsorbent is recycled to said contacting zone.

11. A process according to claim 7 wherein said adsorbent is regenerated by heating to a temperature not above 1000° F. in the presence of air or steam. 90

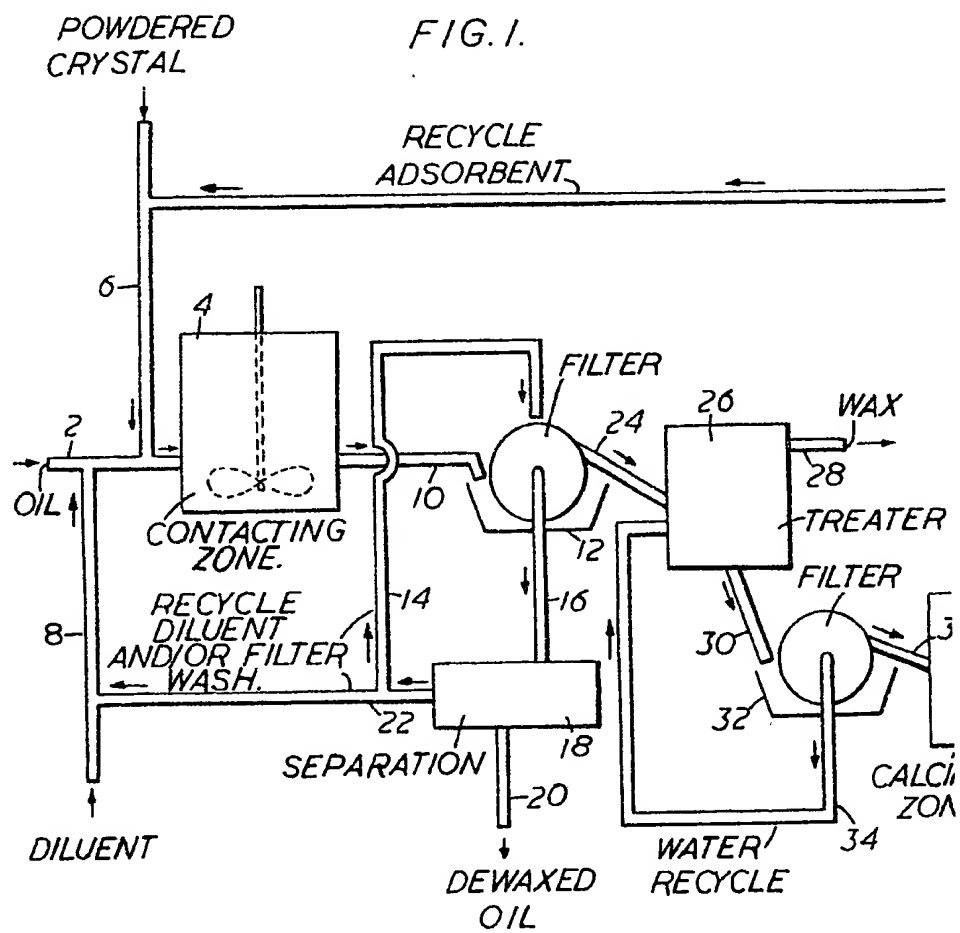
12. A process according to any one of claims 1 to 11 wherein said adsorbent also comprises a crystalline metallic aluminosilicate having pore openings of from 6 to 15 Angstroms. 95

13. A process as claimed in claim 1 substantially as hereinbefore described with particular reference to the examples. 100

14. A process as claimed in claim 1 substantially as hereinbefore described and illustrated in the drawings.

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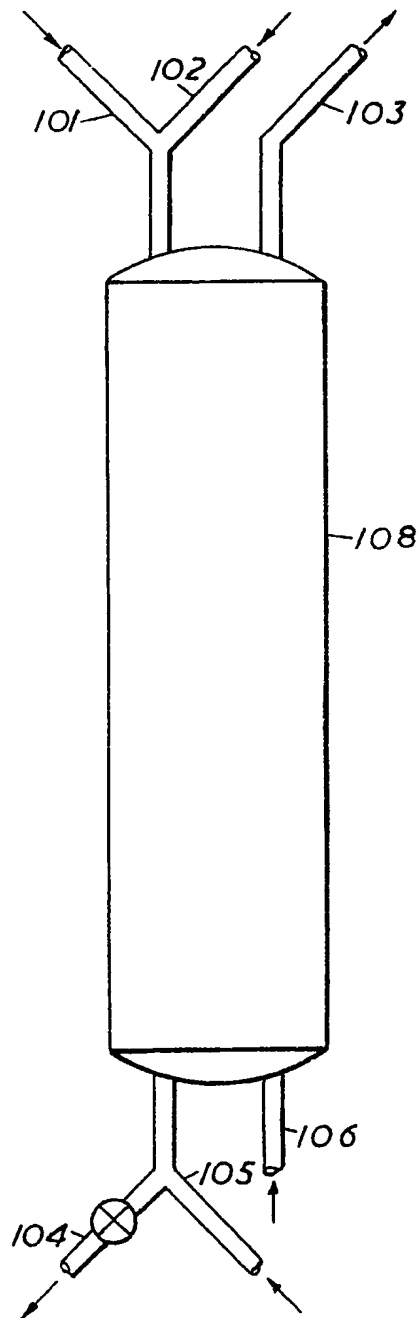
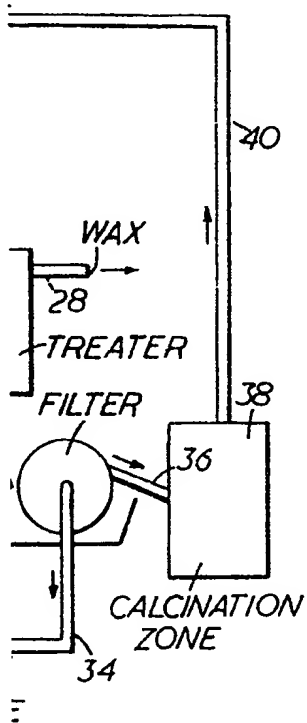
COMPLETE SPECIFICATION

2 SHEETS

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SHEETS 1 & 2

FIG. 2.



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